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OPERATIONAL METHODS OF DEALING WITH CIRCUITS EXCITED BY SINUSOIDAL IMPULSES¹

BY W. B. COULTHARD²

Abstract

A method is developed of deducing operational expressions for complex wave forms such as repeated sinusoidal impulses. By the use of the Heaviside expansion theorem, formulae are obtained for the current flowing in a circuit consisting of a condenser and a loading resistance when fed from a straight line rectifier.

Nowadays, especially in the field of communication engineering, e.m.f.'s having wave shapes much different from sinusoidal shape are used. This paper shows that it is possible to determine the effects of such e.m.f.'s in a circuit by operational methods without resort to Fourier's analysis. Here the output of a rectifier circuit will be considered: of course, the method is applicable equally to waves of any shape. The solution of the differential equations is obtained by means of the Heaviside expansion theorem as being more familiar to engineers, though mathematicians prefer to proceed by using the Bromwich contour integral. In Section (i), methods of obtaining the operational expressions for the impulse and for repeated impulses are developed. This method is based on work by Jeffreys (3). In Sections (ii) and (iii) the result is applied to the output of a rectifier circuit.

(i) Operational Expression for an Impulse and for a Train of Repeated Impulses

From a consideration of Taylor's theorem it can be shown that $e^{-ap}f(t) = f(t - \alpha)$. In circuit theory this means that the switch closure is delayed until a time $t = \alpha$ after the start of count of time, so the function $f(t - \alpha)$ can be written as $e^{-ap}f(t)$. Replacing $f(t)$ by E , we have next an expression as $[e^{-\alpha_1 p} - e^{-\alpha_2 p}]E$. This means that a positive voltage E is applied to the circuit at a time $t = \alpha_1$; at some time later ($t = \alpha_2$) an equal but negative voltage is applied. The resultant voltage impulse is therefore a "square" wave of amplitude E of duration $(\alpha_2 - \alpha_1)$ seconds.

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When the impulse deviates from a constant amplitude the wave form may be regarded as a series of vertical strips. Then

$$(\epsilon^{-\alpha_1 p} - \epsilon^{-\alpha_2 p})f(\alpha_1) + (\epsilon^{-\alpha_2 p} - \epsilon^{-\alpha_3 p})f(\alpha_2) + \dots = E(t),$$

or

$$E(t) = \sum_{r=1}^{\infty} f(\alpha_r) [\epsilon^{-\alpha_r p} - \epsilon^{-\alpha_{r+1} p}].$$

On making the intervals $[\alpha_1 \alpha_2]$, $[\alpha_2 \alpha_3]$, - - - exceedingly small, in the limit we obtain

$$E(t) = - \int_{-\infty}^{\infty} f(\alpha) d[\epsilon^{-\alpha p}].$$

On treating p as a parameter, as in Carson's work, we get on letting

$$E(t) \doteq g(p) \cdot 1$$

that

$$g(p) = \int_{-\infty}^{\infty} p f(\alpha) \epsilon^{-\alpha p} d\alpha.$$

For practical work $f(\alpha)$ vanishes when α is negative so that only the range of α from 0 to $+\infty$ need be considered. We get the Carson integral equation

$$g(p) = \int_0^{\infty} p f(\alpha) \epsilon^{-\alpha p} d\alpha.$$

Likewise for an impulse of limited duration T say, $f(\alpha)$ vanishes when α is greater than T , so follows

$$g(p) = \int_0^T p f(\alpha) \epsilon^{-\alpha p} d\alpha.$$

When the impulse is repeated in the same sense every T seconds, the wave train may be formulated by

$$[1 + \epsilon^{-pT} + \epsilon^{-2pT} + \dots] [\epsilon^{-\alpha_1 p} - \epsilon^{-\alpha_2 p}] E = E(t).$$

By summation

$$E(t) = \frac{\epsilon^{-\alpha_1 p} - \epsilon^{-\alpha_2 p}}{1 - \epsilon^{-pT}} \cdot E,$$

i.e., the operational expression for a repeated unidirectional impulse is obtained by multiplying the operational expression of the impulse by the inverse of $[1 - \epsilon^{-pT}]$. It is readily shown for the case where the impulse is positive and negative alternately that the train is obtained by multiplying by the inverse of $[1 + \epsilon^{-pT}]$.

(ii) Operational Expression for Rectified Sine Waves

We now apply the foregoing theory to the case of rectified sine waves. Consider first the impulse; this is formulated by $E \sin \omega t$ in the interval $[0, \pi]$, so

$$g(p) = p \int_0^{\pi/\omega} \epsilon^{-pt} \sin \omega t dt.$$

On integration this yields $g(p) = \frac{\omega p}{p^2 + \omega^2} \left(1 + \epsilon^{-\pi p/\omega} \right)$.

When this impulse is repeated in the same sense as in a full wave rectifier,

$$g(p) = \frac{\omega p}{p^2 + \omega^2} \cdot \frac{1 + \epsilon^{-\pi p/\omega}}{1 - \epsilon^{-2\pi p/\omega}}.$$

In the case of the single phase rectifier the wave is repeated at intervals of 2π and we get eventually that,

$$g(p) = \frac{\omega p}{p^2 + \omega^2} \cdot \frac{1 + \epsilon^{-\pi p/\omega}}{1 - \epsilon^{-2\pi p/\omega}}.$$

As a final example in this section we consider the case of the chopped wave. Let the wave occur only in the interval $[\delta, \pi - \delta]$. So

$$g(p) = p \int_{\delta/\omega}^{\pi-\delta/\omega} \epsilon^{-pt} \sin \omega t dt.$$

Evaluation of the integral gives, after some work,

$$g(p) = \frac{p^2}{p^2 + \omega^2} \left[\epsilon^{-\delta p/\omega} (\sin \delta + \omega/p \cos \delta) - \epsilon^{-(\pi-\delta)p/\omega} (\sin \delta - \omega/p \cos \delta) \right].$$

This expression is general. On substituting $\delta = \pi/3$ the operational expression for a wave in the interval $[\pi/3, 2\pi/3]$ is obtained as,

$$g(p) = \frac{p^2}{p^2 + \omega^2} \left[\epsilon^{-\pi p/3\omega} \left(\frac{\sqrt{3}}{2} + \omega/2p \right) - \epsilon^{-2\pi p/3\omega} \left(\frac{\sqrt{3}}{2} - \omega/2p \right) \right].$$

This is the operational expression for the "ideal" voltage wave of a three phase rectifier.

(iii) Current Response in a Simple Circuit

From standard theory the operational impedance may be written in the form $Z(p)$ when all the circuit parameters are invariable. The current due to a voltage E . $g(p)$ will be given by the equivalency $i(t) \doteq E g(p)/Z(p)$. Using the arguments developed by Dalzell (2) we have, if

$$g(p) = p \int_0^\infty \epsilon^{-pt} f(t) dt,$$

then by inversion the value of

$$f(t) = \frac{1}{2\pi i} \int_L \frac{g(z)}{z} \epsilon^{zt} dz.$$

So we have here that

$$i(t) = \frac{1}{2\pi i} \int_L E \frac{g(z)}{z} \frac{\epsilon^{zt}}{Z(z)} dz.$$

This contour integral is readily solved in many cases by the Heaviside expansion theorem: in others it is necessary to revert to the original expression for a solution.

To illustrate the procedure we consider some features of a rectifier circuit with a leaky smoothing condenser, whose operational impedance is given by $[R + 1/Cp]$.

(a) For a wave $E \sin \omega t$ in the interval $[0, \pi]$ and zero thereafter acting on the condenser there are the following operational equivalencies for the current:—

In the period $0 < t < \pi/\omega$.

$$i(t) \doteq E \frac{\omega p}{p^2 + \omega^2} \cdot \frac{Cp}{1 + RCp}, \quad (1)$$

where R is the leakage resistance of the condenser and C its capacity. This gives the well known result (1) for the charging current,

$$i(t) = \sqrt{\frac{\omega EC}{1 + \omega^2 R^2 C^2}} \left[\sin \omega t + \phi - \sqrt{\frac{\epsilon^{-\alpha t}}{1 + \omega^2 R^2 C^2}} \right],$$

with $\tan \phi = 1/\omega RC$ and $\alpha = 1/CR$.

For the period $t > \pi/\omega$,

$$i(t) \doteq \frac{E}{R} \frac{\omega p}{p^2 + \omega^2} \cdot \frac{p}{p + \alpha} (1 + \epsilon^{-\pi p/\omega}). \quad (2)$$

Here the effective root is $p = -\alpha$, since the roots $p = \pm j\omega$ have no residue due to the term $(1 + \epsilon^{-\pi p/\omega})$. We have

$$i(t) = - \frac{\omega CE \epsilon^{-\alpha t}}{1 + \omega^2 R^2 C^2} (1 + \epsilon^{\pi \alpha/\omega})$$

as the discharge current.

The exact point of change-over from Condition (1) to Condition (2) requires further investigation, but will not be considered for this particular case.

(b) When the wave $E \sin \omega t$ is repeated in the same sense and is applied to a loading resistance in parallel with a smoothing condenser, we have with I_1 as the current through the condenser, I_2 that through the resistance, and I the total current, on assuming a loss free condenser, that

$$\frac{I_1}{pC} = I_2 R.$$

$$I_1 + I_2 = I.$$

Also

$$I = \frac{E}{R} \cdot \frac{p\omega}{p^2 + \omega^2} \frac{1 + \epsilon^{-\pi p/\omega}}{1 - \epsilon^{-\pi p/\omega}} (1 + RCp).$$

∴

$$I_1 = EC \frac{p^2 \omega}{p^2 + \omega^2} f(\pi p/\omega)$$

and

$$I_2 = \frac{E}{R} \cdot \frac{p\omega}{p^2 + \omega^2} f(\pi p/\omega).$$

These operational expressions show that I_2 is in phase with the voltage whilst I_1 is out of phase by $\pi/2$. Dealing with the case of $t > \pi/\omega$ the load current is obtained, with roots $p = \pm j2n\omega$, as

$$\frac{E}{R} \cdot \frac{2\omega^2}{\omega^2(1 - 4n^2)} \frac{\epsilon^{j2n\omega t}}{\pi} + \frac{2}{\pi} \frac{E}{R} \cdot \frac{\epsilon^{-j2n\omega t}}{1 - 4n^2}$$

The total contribution is

$$\frac{4}{\pi} \frac{E}{R} \frac{\cos 2n\omega t}{1 - 4n^2},$$

where n has values 1 to infinity.

At $p = 0$ the residue is $\frac{2}{\pi} \frac{E}{R}$, and so the total current through the resistance is

$$I_2 = \frac{2}{\pi} \frac{E}{R} \left[1 - 2 \sum_1^{\infty} \frac{\cos 2n\omega t}{4n^2 - 1} \right].$$

In similar manner the current through the condenser is

$$I_1 = \frac{8}{\pi} E\omega C \sum_1^{\infty} \frac{n \sin 2n\omega t}{1 - 4n^2}.$$

From the characteristics of the circuit, certain features, such as the "cut off" and "striking" potentials, can be derived. At some value of ωt the current $I = 0$, i.e., $I_1 = -I_2$. The condenser discharges through the resistance. Let this value of ωt be ψ_2 , defined by:—

$$4\omega CR \sum_1^{\infty} \frac{n \sin 2n\psi_2}{4n^2 - 1} - 1 + 2 \sum_1^{\infty} \frac{\cos 2n\psi_2}{4n^2 - 1} = 0.$$

For values of $\omega t > \psi_2$ the condenser continues to discharge until the applied voltage of the following half wave is equal to that across the condenser. For the condenser discharge,

$$Rpq + q/C = 0,$$

with the boundary condition at $t = 0$, $q = Q_0$. It has been shown (1) under this condition that

$$q \doteq Q_0 \frac{p}{p + 1/CR} = Q_0 e^{-t/CR}.$$

The voltage across the condenser is given by

$$v(t) = \frac{Q_0}{C} e^{-t/CR}.$$

As Q_0/C must be equal to the voltage at cut off we may write

$$v(t) = E \sin \psi_2 e^{-t/CR},$$

with t measured from the instant $\omega t_0 = \psi_2$. When $v(t)$ is equal to the rising voltage of the next half wave of the rectifier, the striking voltage (ψ_1) is defined by

$$E \sin \psi_1 = E \sin \psi_2 e^{-(\pi - \psi_2 + \psi_1)/\omega CR}.$$

(c) We now consider the effects of these discontinuities on rectifier operation. We assume an ideal rectifier, i.e., one having zero forward resistance and an infinite value of the inverse resistance. For the two zones of voltage,

$$g(p) \doteq E \left[p \int_{\psi_1/\omega}^{\psi_2/\omega} e^{-pt} \sin \omega t dt + p \int_{\psi_2/\omega}^{\pi + \psi_1/\omega} e^{-pt} \sin \psi_2 e^{-t/CR} dt \right].$$

We now shift the time axis with ψ_1/ω as zero, then ψ_2 becomes $\psi_2 - \psi_1 = \theta$. On integration

$$g(p) = E \left[\frac{p^2}{p^2 + \omega^2} \left\{ \frac{\omega}{p} - \epsilon^{-\theta p/\omega} \left(\sin \theta + \frac{\omega}{p} \cos \theta \right) \right\} + \sin \theta \frac{p}{p + \alpha} \left\{ \epsilon^{-\overline{p+\alpha\theta}/\omega} - \epsilon^{-\overline{p+\alpha\pi}/\omega} \right\} \right],$$

where $\alpha = 1/CR$.

The term within the first bracket gives the operational expression for the voltage in the interval $[0, \theta]$, while the second term gives that for the interval $[\theta, \pi]$. The load current is now given by

$$i_2 = \frac{E}{R} \frac{g(p)}{1 - \epsilon^{-\pi p/\omega}}.$$

Inspection shows residues at $\pm j\omega$, $\pm j2n\omega$, $-\alpha$ and zero. Evaluation gives after some simplification that

$$i_2 = \frac{E}{\pi R} \left\{ 1 - \cos \theta + \pi - \theta \sin \theta + \sum_1^{\infty} \frac{4n}{1 - 4n^2} \left[\frac{\cos 2n\omega t}{2n} - \frac{\cos \theta \cos 2n(\omega t - \theta)}{2n} + \sin \theta \sin 2n(\omega t - \theta) \right] + 2\omega \sin \theta \sum_1^{\infty} \left[\frac{\epsilon^{-\alpha\theta/\omega} \cos 2n(\omega t - \theta) - \phi_n - \epsilon^{-\alpha\pi/\omega} \cos 2n\omega t - \phi_n}{\sqrt{\alpha^2 + 4n^2\omega^2}} \right] \right\}$$

The second summation term gives the current during the discharge period $[\theta, \pi]$. It will be noted that the current depends *inter alia* on the capacity of the condenser and on the resistance of the load. When the time constant of the circuit is small, the discharge of the condenser is rapid and the voltage thereon may be reduced to zero before the applied voltage reaches zero.

Conclusion

The application of standard operational methods to circuits excited by complex wave forms has been discussed. The solutions are deduced readily even though the mathematics are cumbersome. The solutions are obtained in the form of a series and for calculation purposes the first few terms are sufficient in the majority of cases.

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THE INFLUENCE OF SAMPLE COMPOSITION ON MAGNESIUM, CADMIUM, AND LEAD INTENSITY RATIOS AS RADIATED FROM A SPARK SOURCE¹

BY G. O. LANGSTROTH² AND K. B. NEWBOUND³

Abstract

Marked variations have been observed in the relative intensities of magnesium, cadmium, and lead lines on the addition of various amounts of foreign substances to standard samples and excitation in a condensed spark source. The changes in the interspectra intensity ratios depended on the nature and amount of the added substances, as well as on the elements under consideration. In many instances buffering of the samples with sodium potassium tartrate or potassium nitrate did not reduce the variations. The behaviour cannot be explained solely on the basis of changes in an "effective" discharge temperature. The data permit no obvious generalization that might be helpful as a criterion for the choice of internal standard elements and buffer substances.

Introduction

The accuracy of spectrographic analyses is largely determined by the constancy of the relation between the relative intensities of spectral lines radiated by the source and the amounts of the corresponding elements present in the samples. Spectrographic methods are being applied successfully in the analysis of samples that do not vary markedly in general composition (e.g., alloys). Application in the analysis of samples that do so vary, however, is more difficult if results of high accuracy are desired. This circumstance arises from the fact that the intensity ratio of chosen lines of two elements may depend to some extent on the extraneous composition of the samples. Numerous examples of such a dependence have been noted (1, 2, 5, 9, 10), and special techniques have been developed to deal with it under specific conditions. The general problem however has received little attention, and the factors that must be carefully controlled if such effects are to be minimized remain unknown.

This article describes a preliminary study of the changes that occur in the relative intensities of certain spectral lines when various amounts of foreign substances are added to "standard" samples. The results, over the limited range of these experiments, indicate that the intensity ratio variations depend both on the nature and the amount of the added substance, and are commonly different for different line pairs. In some instances certain ratios tended toward "saturation" values at the greatest additions, but this behaviour was not general. The presence of a buffer did not always improve the constancy of the ratios; it did improve the reproducibility under any particular set of

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conditions. Its efficiency apparently depended on the elements under consideration and on the nature of the change in extraneous composition, as well as on the nature of the buffer itself and the amount used. It has not been possible to generalize the results, and no correlation is apparent between the extent of the intensity changes and the characteristics of the added substances (e.g., ionization potentials of constituents, vapour pressure, stability, etc.). The results cannot be interpreted solely on the basis of changes in an "effective" discharge temperature on the addition of foreign substances (cf. 4). The explanation is probably complex, and must await the compilation of additional data.

Experimental

The sparking circuit proper consisted of a 0.03 microfarad condenser, a 120 microhenry inductance, and a spark gap connected in series. The condenser was connected directly across the secondary of a transformer whose primary voltage was controlled by an auto-transformer. In operation the primary voltage was adjusted to the minimum value consistent with the occurrence of a single spark on every half cycle of the line voltage. The electrodes were of the point-movable-plane type (3); both were copper. The area of the plane electrode was $1.2 \times 1.0 \text{ cm}^2$. An electrode separation of 3.1 mm. was used throughout the work.

Spectra were photographed with a medium quartz spectrograph constructed at the University. For the major part of the work no condensing lens was used. In order to investigate line intensities emitted from different parts of the discharge an image of the source was focused on the spectrograph slit with the aid of a quartz-fluorite lens.

The standard sample contained 0.125, 1.00, and 1.00 mg. per cc. of magnesium, cadmium, and lead respectively (as chlorides). The intensity ratios of chosen lines of these elements were measured with and without the addition of various amounts of extraneous substances. The extraneous substances were the chlorides of potassium, lithium, and calcium, boric acid, and ammonium chloride. These substances were used in amounts that involved comparable numbers of molecules. Similar experiments were carried out with the samples buffered with sodium potassium tartrate, and with potassium nitrate in three different concentrations.

The prepared solution (0.050 cc.) was deposited on the plane electrode and evaporated to dryness under reduced pressure. Deposits that showed appreciable non-uniformity were discarded. The electrode was sparked for 15 sec., during which the spark passed over the entire surface of the plane electrode, tracing out a multiple W pattern and continually striking a fresh surface of the deposit. Some reproducibility was sacrificed in the adoption of this short exposure time, but it was desired that the spark should not strike to some part of the surface whose conditions had been changed by a preceding spark. In some instances sparking periods of 20 and of 25 sec. were used.

A complete series of spectra were photographed on each plate along with plate calibration spectra produced by a step-sector and brass arc. Intensity measurements were made by the usual microphotometric method (7). Since the intensity ratio of two lines differing considerably in wave-length was given in terms of the relative intensities of two lines of the brass arc, comparison of the ratio as given by two plates was permitted only through measurements on spectra common to both. The spectral lines investigated are given in Table I.

TABLE I
SPECTRAL LINES INVESTIGATED*

Emitter	Ground state, cm. ⁻¹	Wave-length, Å	Classification	Initial level, cm. ⁻¹	Final level, cm. ⁻¹
Mg (atom)	61672	2852.1	$3s^2\ ^1S_0 - 3s3p\ ^1P_1^o$	26621	61672
		2779.8	$3s3p\ ^3P_{2,1}^o - 3p^2\ ^3P_{2,1}$	$\begin{cases} 3799 \\ 3840 \end{cases}$	$\begin{cases} 39761 \\ 39801 \end{cases}$
Mg (ion)	121267	2936.5	$3p\ ^3P_{2,2}^o - 4s\ ^2S_{1/2}$	51462	85506
Cd (atom)	72539	3261.1	$5s^2\ ^1S_0 - 5s5p\ ^3P_1^o$	41883	72539
		3403.7	$5s5p\ ^3P_0^o - 5s5d\ ^3D_1$	13052	42425
Pb (atom)	59821	2833.1	$6p^2\ ^3P_0 - 6p(^3P_{1,2})7s\ 2_1^o$	24536	59821
		2614.2	$6p^2\ ^3P_1 - 6p(^3P_{1,2})6d\ 3_1^o$	13754	52004
		3639.6	$6p^2\ ^3P_1 - 6p(^3P_{1,2})7s\ 2_1^o$	24536	52004

* The lines in this table are limited to those for which data are presented in the article.

Results

Typical results are presented in Table II for Mg 2852 Å, Cd 3261 Å, and Pb 2833 Å. The data refer to radiation from the entire discharge, i.e., no condensing lens was used. The symbols A, B, C, D, and E refer to different buffering conditions, as follows:

- A: no buffer was used
- B: sodium potassium tartrate buffer (384×10^{-7} gm. per mm.²)
- C: potassium nitrate buffer (69×10^{-7} gm. per mm.²)
- D: potassium nitrate buffer (138×10^{-7} gm. per mm.²)
- E: potassium nitrate buffer (277×10^{-7} gm. per mm.²)

The amount of buffer is given in mass of salt per square millimetre of electrode. The ratios for the unbuffered sample with no extraneous addition have been set equal to unity, and all other ratios are given in these terms. In each instance the amounts of magnesium chloride, cadmium chloride, and lead chloride per square millimetre of electrode were respectively, 2.0×10^{-7} , 6.8×10^{-7} , and 5.6×10^{-7} gm.—a total salt load of 14.4×10^{-7} gm. per mm.².

TABLE II
EFFECT OF ADDITIONS OF EXTRANEEOUS SALTS ON INTENSITY RATIOS

Additions, mg./mm. ² × 10 ⁷	A No buffer				B Sodium potassium tartrate buffer, 384 × 10 ⁻⁷ gm./mm. ²				C Potassium nitrate buffer, 69 × 10 ⁻⁷ gm./mm. ²				D Potassium nitrate buffer, 138 × 10 ⁻⁷ gm./mm. ²				E Potassium nitrate buffer, 277 × 10 ⁻⁷ gm./mm. ²			
	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Mg	Pb/Mg	Cd/Mg	Pb/Cd	Pb/Cd
None	1.00	1.00	1.00	0.92	0.97	0.82	1.18	1.14	0.70	1.63	1.05	0.59	1.85	1.14	0.52	2.19				
	0.92	1.00	0.92	0.83	—	—	—	1.18	0.76	1.53	1.05	0.50	2.07	1.08	0.45	2.39				
	2.0	0.79	0.95	0.83	—	—	—	1.24	0.72	1.72	1.22	0.59	2.07	1.03	0.45	2.25				
	4.0	0.85	0.95	0.89	0.97	0.76	1.26	1.20	0.72	1.69	1.18	0.60	1.96	1.03	0.45	2.27				
	8.1	1.02	0.96	1.06	0.98	0.79	1.24	1.18	0.67	1.74	1.18	0.49	2.40	1.16	0.46	2.54				
	16.3	1.07	0.93	1.15	0.89	0.72	1.23	1.20	0.70	1.72	1.20	0.47	2.54	1.19	0.41	2.93				
CaCl ₂ · 6H ₂ O	32.6	1.08	0.80	1.35	0.89	0.79	1.13	1.12	0.61	1.82	1.23	0.47	2.60	1.03	0.34	3.02				
	4.5	0.94	1.05	0.90	—	—	—	1.33	0.78	1.69	1.05	0.59	1.78	1.17	0.55	2.25				
	9.1	0.95	—	—	—	—	—	1.30	0.72	1.79	—	0.54	—	1.15	0.54	2.12				
	18.4	0.87	1.10	0.79	0.82	0.83	0.99	1.12	0.73	1.55	1.12	0.59	1.90	1.22	0.55	2.20				
	36.7	0.78	0.75	1.04	0.83	0.80	1.04	1.05	0.70	1.65	1.03	0.55	1.84	1.09	0.51	2.15				
	73.0	0.78	0.80	0.97	0.84	0.70	1.20	0.97	0.70	1.40	0.80	0.49	1.63	0.63	0.46	1.36				
NH ₄ Cl	146.	0.83	0.65	1.28	1.08	0.48	2.25	0.94	0.58	1.60	0.72	0.49	1.46	0.75	0.41	1.82				
	1.1	0.98	1.15	0.85	—	—	—	1.15	—	—	1.09	—	—	1.04	0.52	2.01				
	2.3	0.99	1.08	0.92	—	—	—	1.08	0.71	1.50	1.10	0.55	2.00	1.14	0.51	2.23				
	4.6	0.97	1.00	0.97	—	—	—	1.08	0.75	1.45	1.14	0.67	1.68	1.17	0.51	2.10				
	9.2	1.03	1.20	0.86	0.85	0.73	1.17	1.23	0.68	1.80	1.16	0.62	1.87	1.23	0.52	2.38				
	18.4	1.05	1.00	1.05	0.81	0.81	0.99	1.34	0.71	1.89	1.17	0.64	1.84	1.30	0.86	1.51				
36.7	0.87	0.72	1.20	—	0.77	0.75	1.03	1.32	0.63	2.10	1.29	0.82	1.58	1.41	0.96	1.46				

An analysis of the percentage variations of the ratios given in Table II is presented in Fig. 1. Figs. 2 and 3 present typical data concerning the values of the intensity ratios in light coming from different parts of the discharge for samples of different extraneous composition. Typical data on the behaviour of the intensity ratio of an ionized to a neutral atom spectrum line on addition of extraneous material are given in Fig. 4.

Discussion

Owing to the requirement for a short sparking period in these experiments high reproducibility of results was not attained. The error in the ratios is probably less than 10%, as indicated by repeated measurements on identical samples, but in rare instances it may slightly exceed this value. A plot of the deviations of intensity ratios from the mean for a group of samples differing

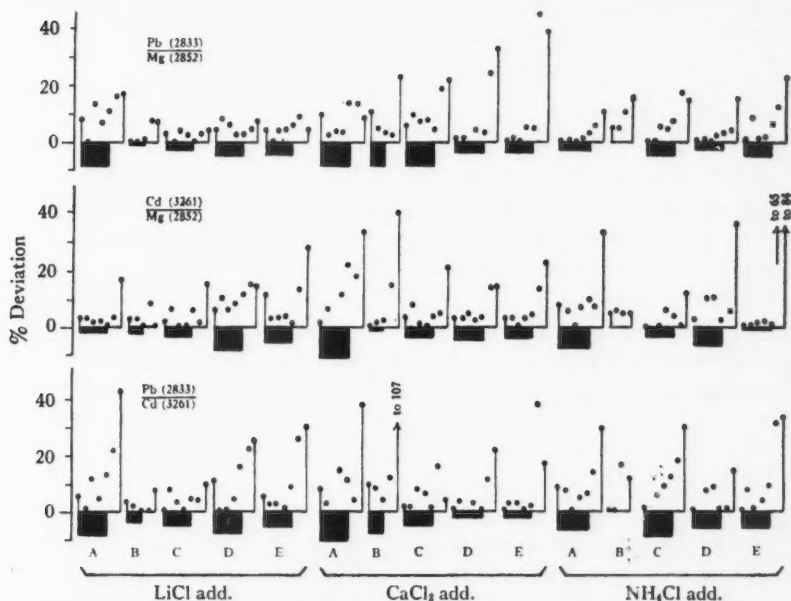


FIG. 1. Percentage variations of intensity ratios from the mean for 'small' additions. The samples are considered in groups, each group consisting of samples buffered in the same way and with the same kind of extraneous material added. The mean value of the intensity ratios for each line pair in each group has been taken as that for 'small' additions (i.e., not greater than 8.1×10^{-7} , 36.7×10^{-7} , and 9.2×10^{-7} gm. per mm.² of lithium chloride, calcium chloride, and ammonium chloride respectively), since in general the larger additions resulted in marked changes in the ratios. The percentage deviation of each ratio in the group from this mean is denoted by a dot above the zero line. The deviations within a group are plotted with additions of extraneous material increasing toward the right; the left-hand dot in each group represents the deviation for the sample with no addition. The depths of the blocks below the zero line represent the average deviation of the ratios for samples with small additions, and their lateral extent indicates the samples included in the mean. The symbols A, B, C, D, and E denote the buffering conditions and have the same significance as in Table II.

only in extraneous composition shows many instances in which the variations in the ratios cannot be attributed to experimental error (Fig. 1). In general, large variations in composition resulted in marked changes in the ratios (Fig. 1 and Table II). Under actual conditions of analysis smaller variations are, perhaps, to be expected, since conditions assumed to give the maximum effect were chosen for these experiments, i.e., the spark continually advanced to a fresh deposit of material. This choice of conditions was made in the hope of ascertaining some of the factors more closely related to the intensity variations.

(a) Results for Unbuffered Solutions

While some of the variations given in Table II, Condition A, are not large, the data show definite trends that are believed to be significant. It has been noted by some workers (2) that certain intensity ratios tend toward "saturation" values as the concentration of a particular substance in the sample is increased. This observation does not appear to hold generally over the range of the present investigation. It does hold in several instances, e.g., with the addition of increasing amounts of potassium nitrate (as a buffer) the Cd/Mg ratio decreased from 1.00 to 0.70 to 0.59 to 0.52 (Table II).

The substances used as additions in these experiments were chosen mainly with respect to the ionization potential of the most easily ionized constituent; they represent a series containing atoms of 4.3, 5.4, 6.1, 8.4, and 13.0 volts ionization potential. The results for the first and fourth of these are not included in the article. The data show no obvious relation between this characteristic and the effect of the addition on the ratios, nor do they suggest any clear cut dependence on other physical characteristics (e.g., vapour pressure, stability, etc.). Furthermore, the effect of an addition depends on the particular line pair under consideration, e.g., addition of the largest amount of lithium chloride used increased the Pb/Cd ratio by 35% but decreased the Cd/Mg ratio by 20%.

(b) Results for Buffered Solutions

A buffer is commonly added to each sample in analysis with the expectation that the character of the discharge will be determined largely by it and so will be little affected by variations in the extraneous composition of the samples. The data of Fig. 1 and Table II indicate that this expectation is not always realized. Whether or not a buffer is effective apparently depends on the line pairs considered and the nature of the variable extraneous material, as well as on the type and amount of buffer salt used. For example, the constancy of the Pb/Mg ratio with "small" lithium chloride additions was improved by either a sodium potassium tartrate or a potassium nitrate buffer, but that of the Cd/Mg ratio deteriorated with the larger potassium nitrate amounts at least. On the other hand, the constancy of the latter ratio was improved by either buffer when "small" calcium chloride, rather than lithium chloride, additions were made. While the use of a buffer is apparently not

always a safeguard against such intensity variations, it has been found to lead to greater reproducibility in the results for any sample of constant composition.

(c) Other Results

The data of Fig. 2 indicate that the interspectra intensity ratios depend on the discharge region from which the examined radiation is emitted. Ratios associated with regions near the point and near the plane electrodes differ from each other and from that associated with radiation from the entire discharge. Moreover the three ratios are not always similarly affected by additions. Such differences might arise either from differences in the concentrations of the elements, or in excitation conditions, at different points in the discharge.

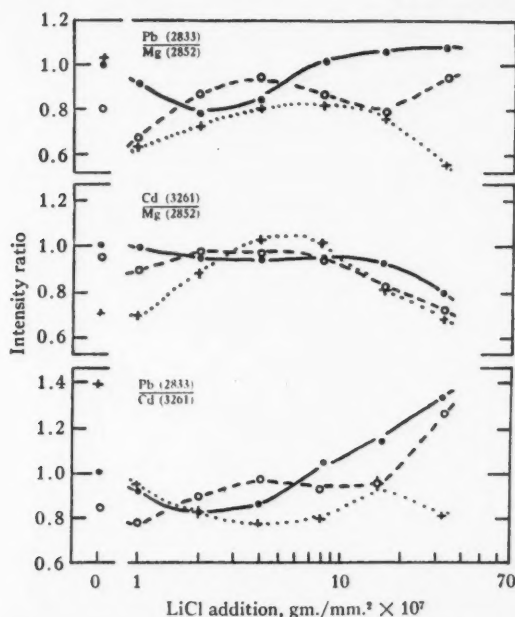


FIG. 2. Comparison of interspectra intensity ratios in light radiated from different parts of the discharge and their dependence on the extraneous composition of the sample. The data, obtained with unbuffered samples, are for the line pairs given in Table II. The ratios for light radiated from regions on the discharge axis near the point and near the plane electrode are denoted respectively by + and \circ . The values for light radiated from the entire discharge are indicated by \bullet .

The data on intraspectrum intensity ratios (Fig. 3) indicate that under some conditions at least there are marked differences in the excitation conditions at different points in the discharge. These differences in excitation are apparently affected by additions to the sample. Consequently, the previous discussion is limited to the particular lines investigated.

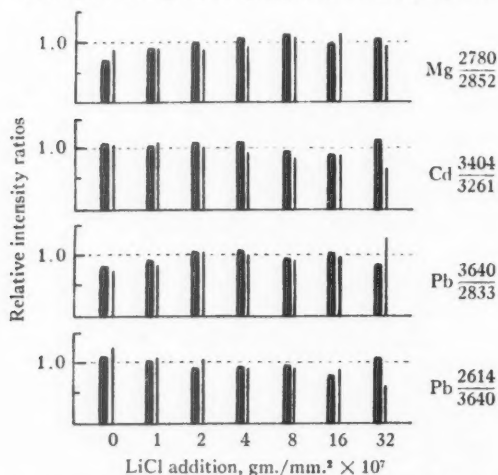


FIG. 3. Comparison of intraspectrum intensity ratios in light radiated from different parts of the discharge, and the changes in their relative values as the extraneous composition of the unbuffered sample was altered. The ratio for light from the entire discharge has been set equal to unity for each sample, and the other ratios are given in these terms. The lengths of the light and heavy lines denote respectively the relative ratios in light radiated from regions on the discharge axis near the point and near the plane electrode.

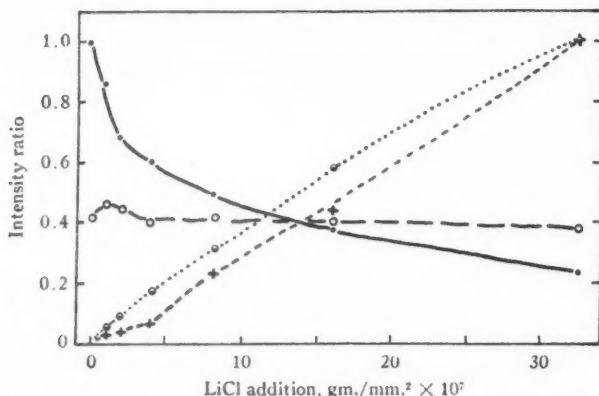


FIG. 4. Behaviour of the intensity ratio of a line of the ionized to a line of the neutral atom spectrum on addition of extraneous material to the sample. \bullet and \circ denote respectively the ratios $\text{Mg II}/\text{Mg I}$ ($2937 \text{ \AA}/2780 \text{ \AA}$) for unbuffered and for buffered (potassium nitrate) samples. $+$ and \circ denote respectively the ratios $\text{Li I}/\text{Mg I}$ ($4603 \text{ \AA}/2780 \text{ \AA}$) for the same samples, unbuffered and buffered. The latter values are plotted to give some indication of the relative amounts of lithium actually getting into the discharge for various lithium chloride additions to the sample.

Fig. 4 shows the typical decrease that occurs in the intensity ratio of ion to neutral atom lines when additions are made to an unbuffered sample. The curve is qualitatively that expected from Saha's theory of thermal

ionization (8). As applied to mixed vapours (cf. 6) theory predicts that such ratios should decrease on the addition of more easily ionized atoms to the discharge. The fact that the corresponding curve for calcium chloride additions (not presented) showed a more rapid decrease in the ratio is understandable since the Ca I/Mg I ratio showed a much steeper initial increase than the Li I/Mg I ratio, i.e., the partial pressure of Ca in the discharge increased more rapidly than that of Li in the initial stages. The virtually constant value of the Mg II/Mg I ratio obtained with the buffered sample is likewise to be expected, since the buffer supplies relatively large numbers of K atoms (ionization potential, 4.3 volts) to the discharge at all times. It may be pointed out that this interpretation of the data does not assume a decrease in the effective temperature of the discharge on addition of extraneous material; it involves consideration of partial pressures and ionization potentials only.

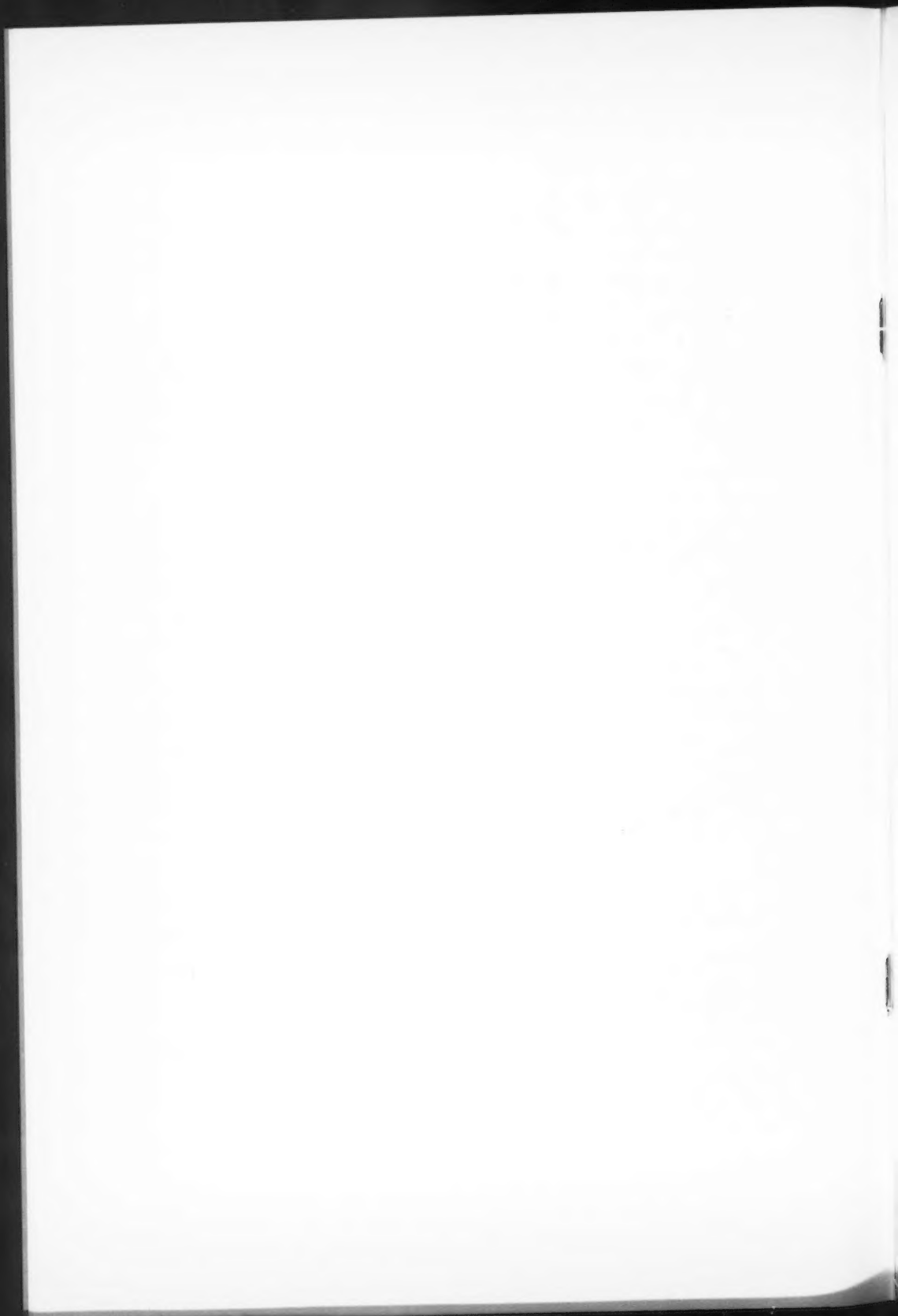
(d) *Remarks*

The observed changes in intraspectrum intensity ratios (and hence those in interspectra ratios) cannot be interpreted solely on the assumption of a decrease in "effective" discharge temperature (cf. 4). The decrease in the Mg II/Mg I ratio for the buffered sample of Fig. 4 would require a change of about 10° K in the temperature; this is far too small to account for observed changes in the ratios of lines of the neutral atom. Moreover, in some instances the changes in two different ratios require temperature changes in opposite directions.

It is doubtful that the concept of an "effective" temperature has any real meaning with respect to the details of intensity variations in these experiments. Intensity ratios in light taken from the entire discharge are results integrated over a region in which point values differ. Furthermore, they are time-integrated results. This may be an important feature when interspectra ratios are under consideration, since transport phenomena for different elements are involved. The data of this investigation have not led to any interpretation of the intensity variations in terms of source mechanisms.

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THE ALKALOIDS OF PAPAVERACEOUS PLANTS

XXXII. *STYLOPHORUM DIPHYLLUM* (MICHX.) NUTT., *DICRANOSTIGMA FRANCHETIANUM* (PRAIN) FEDDE AND *GLAUCIUM SERPIERI* HELDR.¹

BY RICHARD H. F. MANSKE²

Abstract

The only alkaloids found in *Stylophorum diphyllum* and in *Dicranostigma franchetianum* were protopine, chelidonine, and stylopine. It is concluded that there is no chemical justification for allocating separate generic rank to these plants. *Glaucium serpierei* yielded protopine, glaucine, isocorydine, and aurotensine. Luteanine, present in *G. flavum*, could not be found. In addition there was present a small amount of phenolic base which on methylation yielded sinactine. It is concluded that the plant probably deserves specific rather than varietal rank.

The alkaloids of *Stylophorum diphyllum* (Michx.) Nutt. were isolated in 1901 by Schlotterbeck and Watkins (6) who reported the presence of protopine, chelidonine, sanguinarine, stylopine, and diphylline. In a previous communication (4) the author pointed out that stylopine is $C_{19}H_{17}O_4N$ and not $C_{19}H_{19}O_4N$ as reported by the authors already quoted. The *dl*-form is identical with bis-methylenedioxy-tetrahydro-protoberberine and melts at $221^\circ C.$ *, whereas the *l*-form melts at $202^\circ C$. The author has previously recorded the occurrence of the *dl*-form (1) and a mixture, not separated, of the *l*- and *dl*-forms (2, 4). It is probable that diphylline is in fact *dl*-stylopine, although no trace of it has been found in this investigation. Sanguinarine as known in 1901 was inadequately characterized and has since been shown to consist of at least two bases, the more readily obtainable of which is chelerythrine. During the examination of another plant, the author has had occasion to isolate and characterize chelerythrine but it could not be found in *S. diphyllum*. The yellow colour of the sap of the plant is not due to a coloured alkaloid but to a mixture of highly oxygenated compounds which, however, were not obtained pure. The genus *Dicranostigma* as now recognized comprises three species, all native to Asia. It was at one time regarded as *Stylophorum*. The species now reported upon, *D. franchetianum* (Prain) Fedde, was found to contain only three alkaloids and the same three only were obtained from *S. diphyllum*, namely, protopine, chelidonine, and stylopine. The only chemical difference was that the last alkaloid was present in the

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* All melting points are corrected.

dl-form. It would appear from this observation that the chemical constituents so characteristic of the species in the subfamily Fumarioideae are not necessarily of the same degree of specificity in other genera or species. Nevertheless it is concluded that, in view of the chemical similarity between the two plants, there is no adequate justification for their separation into two genera.

In this connection an examination of *Glaucium serpioides* Heldr. is of interest. This plant is frequently regarded as a variety of *G. flavum* Crantz., namely var. *serpioides* Halaczky. It was found that the two plants each contained the following alkaloids,—protopine, glaucine, isocorydine, and aurotensine. The presence of luteanine (3) in *G. serpioides* could, however, not be demonstrated. There was obtained a small amount of an amorphous base which on methylation with diazomethane yielded an alkaloid identical with a partly racemic sinactine, first obtained from *Fumaria officinalis* (1). It appears therefore that the phenolic precursor is either cheilanthifoline (5) or an isomer. It is not likely that such a base was overlooked in the previous exhaustive examination of *G. flavum*.

Experimental

There was available for these investigations the following amounts of dried and ground material—*S. diphyllum*—4.0 kg. (roots); *D. franchetianum*—8.65 kg.; and *G. serpioides*—4.82 kg. All material was grown in a local garden. The *Stylophorum* was collected in autumn when the plants were dormant, and the following record refers only to the roots although the leaves collected in summer were also examined. They contained only very small amounts of the same bases. The other plant material was collected during the flowering period before any seed had ripened.

The procedure adopted in the three cases was the same and followed that repeatedly used by the author.

Protopine and Chelidonine

Protopine and chelidonine occur together in the non-phenolic fraction (BS) (hydrochlorides not extracted from aqueous solution by means of chloroform). The protopine from *G. serpioides* was readily obtained in a pure condition and the presence of other bases, except in traces, is improbable.

The separation of protopine and chelidonine can be easily effected by the following procedure, which is almost quantitative and was here employed. The dried mixture of bases is dissolved in hot methanol and the filtered solution inoculated with a crystal of protopine. The chelidonine is readily soluble in methanol and the protopine which crystallizes may be further purified via its hydrobromide or by direct crystallization from chloroform-methanol. It was present to the extent of about 0.03% in both *S. diphyllum* and *D. franchetianum*.

The methanolic mother liquor from the protopine is acidified with dilute hydrochloric acid, the methanol boiled off, and the filtered solution allowed to cool. The sparingly soluble hydrochloride of chelidonine then crystallizes. It is preferably recrystallized once from hot water and the free base is then

regenerated by adding an excess of ammonia to a rapidly cooled aqueous solution of the salt. The washed and dried precipitate is dissolved in methanol and the solution evaporated to a thin syrup. An excess of dry ether is added, the resulting turbid solution filtered, and the filtrate evaporated to a small volume. Seeding with a crystal induces immediate crystallization of stout highly refracting prisms of chelidonine, which melt at 135 to 136° C. The maximum melting point of 137° C. is attained by one recrystallization. The yield was 0.02% from *D. franchetianum* and 0.05% from *S. diphyllum*. In admixture with an authentic specimen of chelidonine, prepared from *Chelidonium majus* L. by the same procedure, the alkaloid obtained from the above sources showed no depression in melting points.

Stylophine

The non-phenolic fractions (BC) from the *Stylophorum* and the *Dicranostigma* yielded sparingly soluble hydrochlorides from which the free bases were regenerated. They were then recrystallized from hot methanol. The former yielded *l*-stylophine melting at 202° C. The latter yielded the less soluble *dl*-stylophine melting at 221° C. either alone or in admixture with a specimen of *dl*-stylophine from *F. officinalis* (1). The mother liquors in this case yielded a less pure base melting at 206° C., which proved to be identical with the partly racemic stylophine obtained from *C. claviculata* (4).

The presence of phenolic bases in these two plants could not be demonstrated.

Glaucine

The glaucine was isolated as in the case of *G. flavum* (3). Exhaustive examination of the mother liquors failed to yield luteanine, and other bases were absent except in possible traces.

Isocorydine

The phenolic fraction (EC) was freed of contaminating non-phenolic bases by redissolving in dilute acid and adding an excess of potassium hydroxide. The filtered aqueous solution was saturated with carbon dioxide and extracted with ether. The washed ethereal solution was evaporated to a small volume, filtered to remove a turbidity, and concentrated to a thin syrup, which almost immediately deposited colourless stout prisms of isocorydine. The base melted at 185° C. either alone or in admixture with an authentic specimen of isocorydine. The yield was 0.004%.

Aurotensine

The combined phenolic fractions (BSE and FES) were obtained by extracting the carbonated solution with ether. The residue from the ether extract crystallized readily in contact with a small volume of methanol. The characteristic plates thus obtained melted at 128° C., and this melting point was not lowered when the base was admixed with a specimen of aurotensine. The yield was about 0.002%, including a small amount recovered from the mother liquor as hydrochloride.

There remained a small amount of alkaloid that could not be obtained crystalline either as free base or as hydrochloride. It was methylated with diazomethane and the non-phenolic base converted to its hydrochloride, which was sparingly soluble in water or methanol. The regenerated base was recrystallized from methanol, and it then consisted of colourless fine needles melting sharply at 117° C. In admixture with a specimen of sinactine from *F. officinalis*, it melted at the same temperature.

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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XXXIII. *CORYDALIS CHEILANTHEIFOLIA* HEMSL.¹BY RICHARD H. F. MANSKE²

Abstract

Corydalis cheilantheifolia Hemsl. was found to contain the following alkaloids,—*l*-canadine, stylopine, *l*-corypalmine, *l*-cheilanthifoline, protopine, and allo-cryptopine. It is pointed out that the presence of these alkaloids is evidence of the close relation of this plant to *C. ophiocarpa*. Incidentally, further proof for the constitution of ophiocarpine, previously given, has been obtained by oxidation to a corydaldine.

Corydalis cheilantheifolia Hemsl. (*C. daucifolia* Léveillé et Vaniot), as its name indicates, is the fern-leaved *Corydalis* (from *Cheilanthes* Sw., a genus of ferns). It is botanically related to *C. ophiocarpa*, being placed in the same subsection, and indeed its natural habitat overlaps that of the latter. It is native to China in the provinces of Hupeh, Szechwan, and Kweichow.

The chemical constituents resemble most closely those of *C. ophiocarpa* Hook. f. et Thoms. (3). The following alkaloids are common to both plants,—protopine, allo-cryptopine, *l*-canadine, berberine, *l*-corypalmine, and *l*-stylopine (previously reported as alkaloid F40). In addition to these alkaloids, *C. cheilantheifolia* contains cheilanthifoline (4), *dl*-stylopine, and a non-basic nitrogenous substance which yields analytical figures in fair agreement with $C_{21}H_{18}O_8N_2$. Ophiocarpine, an alkaloid thus far obtained only from *C. ophiocarpa*, could not be isolated from the plant under discussion. The correctness of the constitution of this alkaloid as previously given (3) was confirmed by the simple expedient of oxidizing it with permanganate to 6 : 7-methylenedioxy-1-keto-1 : 2 : 3 : 4-tetrahydro-isoquinoline. This is proof that the hydroxyl group cannot be in positions 5 or 6.

Experimental

The material was grown in a local garden and consisted almost entirely of the first year's growth. The plant is a facultative biennial but not entirely winter hardy in this locality. There was available a total of 8.6 kg. of which the roots constituted only 0.4 kg. Considerable difficulty was encountered in obtaining satisfactory separation and purification of the alkaloids, and it is probable that the examination of a larger amount of material will disclose the presence of a number of other alkaloids.

The following is a summary of the various fractions and the contained alkaloids.

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² Chemist.

Base hydrochlorides extracted from aqueous solution by means of chloroform:—

BC—Non-phenolic bases,—*l*-canadine, *l*- and *dl*-stylophine.

BCE + EEC—Phenolic bases,—*l*-corypalmine, cheilanthifoline.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—protopine, allo-cryptopine.

BSE + EES—Phenolic bases,—(not crystallized).

l-Canadine and Berberine

The non-phenolic base mixture (BC) was redissolved in a large volume of dilute hydrochloric acid and the filtered solution cooled. The sparingly soluble salt that separated was recrystallized from hot water. It was then dissolved in hot water and the rapidly cooled solution basified with ammonia. The precipitated base was recrystallized from hot methanol; it then melted, either alone or in admixture with a specimen of *l*-canadine, at $135^{\circ}\text{C}.$ * $[\alpha]_D^{22} - 317^{\circ}$ ($c = 0.4$ in methanol).

The ammoniacal filtrate from the canadine was acidified with acetic acid and heated with zinc dust until the yellow colour had faded. The addition of ammonia and extraction with ether yielded a base which when recrystallized from methanol melted sharply at $170^{\circ}\text{C}.$ Its identity with *dl*-canadine was proved by a mixed melting point determination, and therefore the ammonia soluble base was berberine.

dl- and *l*-Stylophine

The mother liquor from the crystallization of the canadine and berberine hydrochlorides was basified with ammonia and the precipitated bases were washed thoroughly with water to remove the remaining quaternary salts. The dried product was recrystallized a number of times from methanol. There was ultimately obtained a base that proved to be identical with a specimen of *dl*-stylophine (5) melting at $220^{\circ}\text{C}.$

The more soluble fractions were reconverted to hydrochlorides and these recrystallized from hot water. A small amount of *l*-canadine hydrochloride was first obtained. The more soluble but crystallized salt was converted to free base, which was extracted with hot methanol. The less soluble portion consisted substantially of *dl*-stylophine. The extract on slight concentration and cooling deposited colourless fragile needles melting at $196^{\circ}\text{C}.$ In admixture with a specimen of alkaloid F40 from *C. ophiocarpa* it melted at the same temperature. Found: C, 70.15, 70.45; H, 5.43, 5.38; N, 4.91, 4.90%. Calc. for $\text{C}_{19}\text{H}_{17}\text{O}_4\text{N}$: C, 70.59; H, 5.26; N, 4.33%.

Further crystallization did not materially increase the melting point, but in admixture with a specimen of *l*-stylophine from *Stylophorum diphyllum* (5) it melted indefinitely at $200^{\circ}\text{C}.$ It was positively characterized as stylophine by conversion to the *dl*-form melting at $221^{\circ}\text{C}.$ This was accomplished by

* All melting points are corrected.

the usual procedure of oxidation first with alcoholic iodine and subsequent reduction with zinc and acetic acid.

l-Corypalmine and l-Cheilanthifoline

The fractions (EEC and BCE) and the completely phenolic component of (EC) in contact with methanol crystallized readily. When recrystallized from chloroform-methanol it melted at 230° C. and at the same temperature in admixture with specimens of *l-corypalmine* from other sources.

The methanolic mother liquor from which the above base had been crystallized was evaporated to a small volume and treated with methanolic hydrogen chloride. The sparingly soluble salt which separated was washed with acetone and converted to free base by treating in aqueous solution with ammonia. The base, *l-cheilanthifoline*, crystallized readily from hot methanol and melted at 184° C. Further crystallization did not raise the melting point. It proved to be identical with the same base obtained from *C. scouleri* (1) and *C. sibirica* (2). Yield, 20 p.p.m.

Protopine and Allo-cryptopine

The fraction (BS) was dissolved in chloroform, the solution was filtered and evaporated, and the residue dissolved in hot methanol. The addition of a crystal of protopine induced the immediate crystallization of the same alkaloid. It was readily obtained pure by recrystallization from chloroform-methanol (m.p. 210° C.). The yield of protopine was 0.14% from the aerial portion and 0.74% from the roots, the latter figure being almost as high as the corresponding one for *C. sibirica*.

The combined mother liquors were evaporated to a small volume and a further small amount of protopine crystallized out. Some methanol was added and the solution filtered with the aid of charcoal. The addition of a crystal of allo-cryptopine induced immediate crystallization of this base. It was obtained pure by recrystallization from hot methanol, which served to eliminate a small amount of protopine still present. The yield of allo-cryptopine (m.p. 160° C.) was about 0.06%.

Neutral Nitrogenous Substance

The methanolic extract of the roots was treated with dilute hydrochloric acid and the insoluble portion filtered off. The filtrate deposited a crust of yellow crystalline material in the course of several days. It was filtered off, washed with warm water, and recrystallized from much boiling water. It was then washed with methanol, in which it is virtually insoluble, and recrystallized once more from hot water. As thus obtained it consisted of dark brown glistening prisms, which neither melted nor showed any evidence of decomposition at 360° C. It contained neither halogen nor methoxyl and was virtually ash free. Found: C, 58.99, 58.95; H, 4.19, 4.07; N, 6.53, 6.55%. Calc. for $C_{21}H_{18}O_8N_2$: C, 59.12; H, 4.23; N, 6.58%.

Oxidation of Ophiocarpine

A solution of the base (0.5 gm.) in 50 cc. of water containing a drop of hydrochloric acid was neutralized to incipient turbidity with sodium carbonate and treated with a cooled aqueous solution of potassium permanganate (0.9 gm.). When the last had been reduced, a pellet of potassium hydroxide was added, and the heated solution filtered. It was cooled and extracted with ether. The residue from the ether was boiled with a little water, the solution cooled, filtered, and extracted with ether. The residue from this extract was sublimed *in vacuo* and thus obtained in brilliant colourless prisms melting at 183° C. In admixture with a specimen of 6 : 7-methylenedioxy-1-keto-1 : 2 : 3 : 4-tetrahydro-isoquinoline similarly prepared from canadine it melted at the same temperature.

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COLUMN PACKING AND THE SEPARATION OF ISOTOPES¹

BY H. G. THODE² AND F. O. WALKLING³

Abstract

An expanded shale aggregate packing material for fractionating columns has been investigated. The new packing is inert, cheap, and easily wetted by water. Columns packed with this material have been tested in the distillation of hydrocarbons and with water systems. The results indicate that the new packing compares favourably, both with regard to efficiency and throughput, with other column packings and is more efficient with water systems. It should have industrial applications as well as applications in the separation of isotopes.

Introduction

For the past two years the writers have been interested in developing a cheap and efficient column packing for use in the separation of isotopes by distillation and chemical exchange methods. During the course of this work a column packing has been investigated which seems to have applications in columns of large diameter for the separation of isotopes. This packing material is cheap, compares favourably with other packings in the separation of hydrocarbons and is particularly efficient with water systems, probably owing to its exceptional wetting properties. Because this new packing may have applications in the separation of isotopes and also because a cheap and efficient packing may have wide application in industrial processes this report of the preliminary investigations is presented.

Columns using stainless steel gauze (6) and aluminum turnings (4) have been used in the separation of oxygen isotopes by the distillation of water, but have not given good results. The Pegram rotating column (2) was more effective but has other disadvantages. The writers have used a 60 ft. column 1 in. in diameter, packed with 5 mm. glass helices, obtaining a 3.5-fold change in the ratio of oxygen isotopes. However, the results were disappointing in view of the high efficiencies obtained when the columns are used for the separation of hydrocarbons. In order to produce larger quantities and higher concentrations of the O^{18} isotope, larger columns are required using the cascade system of Thode and Urey (7). In this system, concentrated material from a column of larger diameter is fed into a column of smaller diameter. It is for these columns of larger diameter that a very efficient and cheap packing is required, as their large volume makes the cost of the more expensive type of packing prohibitive.

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Experimental and Results

The packing material was prepared by the Cookville Co. from a special shale*. Crushed shale is passed through a furnace at 2700° F., which is well above the melting point of the shale. Carbon dioxide is formed owing to the presence of small amounts of carbonates, and an expanded clinker is produced. These clinkers are then crushed, cleaned, and graded according to particle size. The resulting aggregates are used as packing in the columns. The irregular shape of the aggregate particles prevents close packing, and the honeycomb surface results in a large surface area. The approximate chemical composition is given in Table I. The calcium, magnesium, and iron are probably present as monosilicates, which would account for the exceedingly low chemical activity of the packing.

TABLE I
CHEMICAL ANALYSIS OF SHALE AGGREGATE PACKING, %

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	Loss on ignition
64.12	21.34	8.20	3.10	2.60	0.45	0.15

The columns packed with shale aggregate have been tested on three different systems; carbon-tetrachloride-benzene, the distillation of water, and a chemical exchange process. In all cases the columns were packed by pouring the loose material into the top of the column so that it fell at random. In the apparatus used for the first two systems, the column was insulated with two layers of heavy asbestos paper and two layers of crumpled aluminum foil; the auxiliary equipment, boiler, condenser, etc., were of standard design. Provision was made for the removal of samples from each end of the column.

Carbon-tetrachloride-benzene

At the start of each run a sufficient quantity of carbon-tetrachloride-benzene mixture was introduced into the boiler by pouring the liquid through the top of the column. This procedure was followed to ensure complete wetting of the packing. The mixture was then boiled at a constant rate with total reflux of vapour at the top. Samples were removed from the column every 30 min. and were analysed by the refractive index method, data from the International Critical Tables being used (3, p. 77). This procedure was continued until the analysis indicated that the column had reached a steady state. The concentration range used was so chosen as to obtain the most accurate plate efficiency data.

Several runs were made with each packing. The results obtained with glass helices, carborundum, corundum and five different grades of shale aggregate packings are given in Table II. The number of theoretical plates in Column 7 was determined graphically by means of the equilibrium data of

* Dundas shale, used by the Cookville Company for the manufacture of "Haydite" aggregate.

Rosanoff and Easley (5, p. 971) for carbon-tetrachloride-benzene mixtures. The H.E.T.P. (height equivalent to a theoretical plate) is obtained by dividing the length of the column by the number of theoretical plates. †

TABLE II
COMPARISON OF VARIOUS TYPES OF COLUMN PACKING ON HYDROCARBONS

Packing		Free space, %	Rate of flow, litres/hr.	Mole % CCl ₄		Total theoretical plates	H.E.T.P., cm. (in.)
Type	Grade			Top	Bottom		
Shale aggregate	2-3 mesh	52.2	1.36	45.3	12.3	12.0	8.3 (3.3)
				44.5	11.8	12.0	8.3 (3.3)
Shale aggregate	4-6 mesh	53.8	1.26	55.8	6.5	20.0	5.0 (2.0)
				57.2	7.6	19.5	5.0 (2.0)
Shale aggregate	6-8 mesh	55.6	1.14	66.5	9.3	24.0	4.2 (1.7)
				63.6	7.3	23.5	4.3 (1.7)
Shale aggregate	8-10 mesh	—	1.20	65.3	7.3	24.5	4.1 (1.6)
				0.60	67.3	6.1	26.7
Shale aggregate	10-12 mesh	—	1.00	67.8	9.8	24.7	4.0 (1.6)
				59.2	6.1	22.2	4.1 (1.8)
Glass helices	5 mm. × .5 mm.	80.	—	54.6	10.6	16.5	6.1 (2.4)
				48.0	9.8	15.2	6.6 (2.6)
Carborundum	10 mesh	—	0.84	44.5	2.2	20.5	4.9 (1.9)
				47.2	3.6	19.5	5.1 (2.0)
Corundum	8 mesh	47.	—	36.0	7.3	12.7	7.9 (3.1)

Column 40 in. long, I.D. 1.5 in. Operated under total reflux.

The shale aggregate is very efficient and compares favourably with the glass helix packing developed by Fenske. Optimum efficiency is obtained with the 8-10 mesh grade of aggregate packing. However, coarser packing can be used without much loss in efficiency, with the advantage of a lower resistance to vapour flow. The back pressure of a 1 in. column 60 ft. long packed with 3-4 mesh shale aggregate was the same as a similar column packed with 5 mm. glass helices. The columns were operated on the distillation of water with a pressure of 5 cm. of mercury at the top and a rate of flow of 3.8 cc. per min. giving a back pressure of 10 cm. In some processes the throughput of the column will be limited not by the flooding velocities (which are relatively high) but by the maximum permissible back pressure. There is little change in efficiency with increase in column diameter from 1.5 to 3 in. (see Table III). Fenske reports similar results with columns packed with glass helices.

TABLE III
 VARIATION OF EFFICIENCY OF SHALE AGGREGATE PACKING WITH COLUMN DIAMETER
 (Tests on 4-10 mesh packing)

Carbon-tetrachloride-benzene system					
Inside diameter of column, in.	Rate of flow, litres/hr.	Mole % CCl_4		No. of theoretical plates	H.E.T.P., cm. (in.)
		Top	Bottom		
1.5	0.5	60.4	6.7	23.3	4.4 (1.7)
2.84	3.0	54.8	6.4	19.4	5.2 (2.1)
2.84	3.0	61.6	6.6	22.2	4.6 (1.8)

$\text{H}_2\text{O}^{16} - \text{H}_2\text{O}^{18}$ system					
Inside diameter of column, in.	Rate of flow, litres/hr.	Mole % H_2O^{18}		No. of theoretical plates	H.E.T.P., cm. (in.)
		Top	Bottom		
1.5	0.3	.178	.206	48.8	2.1 (.83)
2.84	1.5	.192	.222	48.5	2.2 (.86)

Columns 40 in. long. Operated under total reflux.

Distillation of Water

In the distillation of water, as in the separation of carbon tetrachloride and benzene, the apparatus was operated under total reflux with a large reservoir of liquid in the boiler, until a steady state was reached. Water samples were removed from the top and bottom of the column. By the method of Cohn and Urey (1) these samples were brought to isotopic equilibrium with carbon dioxide, which was then analysed with a mass spectrometer. The mole fraction of O^{18} as determined by this method is accurate to $\pm 1\%$. The number of theoretical plates, k , in the column at equilibrium and operating under total reflux is defined by the equation:

$$\frac{\frac{n}{1-n}}{\frac{N}{1-N}} = \alpha^k, \quad (1)$$

where N and n are the mole fractions of O^{18} at the top and bottom of the column respectively, and α is the simple process separation factor.

Two tests have been made with the columns packed with shale aggregate. The results are given in Table III. In calculating the number of theoretical plates, α was taken as 1.003 at 100°C ., a value obtained experimentally by Wahl and Urey (9).

The results are very encouraging and indicate that the new packing is very efficient in the separation of the oxygen isotopes by the distillation of water. As in the hydrocarbon runs, the 3 in. column is as efficient as the 1.5 in. column. The liquid holdup per unit length was found to be about double that of the columns packed with glass helices. However, the indications are that the holdup per plate will be less in the columns of larger diameter. More extensive tests are now in progress.

Chemical Exchange Process

The chemical exchange process used by H. C. Urey and his co-workers for the separation of the nitrogen isotopes (7) has been discussed in detail. The process depends on an exchange between ammonium nitrate solution and ammonia gas. A 60% solution (by weight) of ammonium nitrate is pumped into the top of a fractioning column, *F*, at a constant rate (Fig. 1). This solution

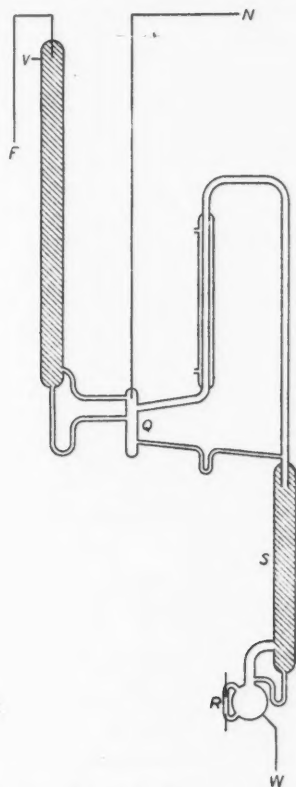


FIG. 1. Chemical exchange apparatus.

TABLE IV
COMPARISON OF VARIOUS TYPES OF COLUMN PACKING ON CHEMICAL EXCHANGE

Packing	Length, cm.	I.D., cm.	Rate of flow, cc./min.	N ¹⁵ enrichment factor	No. of theoretical plates	H.E.T.P., cm. (in.)	Holdup per plate, cc.
Stedman stainless steel gauze	92.0	2.5	2.5	1.18	7.2	12.7 (4.8)	5.0
Stedman stainless steel gauze	92.0	2.5	2.5	1.17	6.9	13.3 (5.2)	5.0
Glass helices, 5 mm.	120.0	1.0	0.65	1.42	15.3	7.8 (3.3)	—
Glass helices, 6 mm.	130.0	2.2	2.5	1.29	11.2	11.6 (4.6)	4.1
Glass helices, 6 mm.	130.0	2.2	6.3 10.0*	1.31	11.8	11.0 (4.3)	4.1
Berl saddles, 6 mm.	130.0	2.2	5.0	1.19	7.6	17.1 (6.7)	6.6
Berl saddles, 6 mm.	170.0	7.0	50.0	1.22	8.7	19.6 (7.6)	—
Berl saddles, 6 mm.	170.0	7.0	80.0	1.24	9.4	18.1 (7.1)	—
Shale aggregate, 3 mm.	100.0	2.5	6.5 11.0*	1.46	16.6	6.0 (2.4)	5.4

* Flooding velocity.

drains to the foot of the column to the reaction chamber, Q , where alkali is added, N , to liberate the ammonia. The ammonia is then stripped from the waste solution by means of the stripper, S , and boiler, R , returning to the column where it flows to the top, counter current to the solution and escapes to a stripper and vacuum pump at, V . Since N^{15} is favoured in the liquid phase there is a net transport of N^{15} toward the foot of the column, where it concentrates. The apparatus is operated at a pressure of 10 cm. of mercury and at room temperature. For this system the number of theoretical plates, k , in a column at equilibrium and operating at total reflux is defined by Equation (1), where N and n are the mole fractions of N^{15} at the top and bottom of the column, respectively.

This process calls for a large number of theoretical plates, as α differs only slightly from unity (approximately 1.023) (8). Also, owing to the low initial concentration and the low rate of transport, columns with a small holdup must be used. Those with a large number of theoretical plates may require several months to reach a steady state even when they have a low holdup. However, by using a cascade system of columns such that a column of small diameter operates on concentrated material from a column of larger diameter, the time required to reach a given concentration can be reduced. It is for these columns of relatively large diameter that a cheap and efficient packing material is especially required. Since the nitrogen process is typical of chemical exchange processes involving water solutions, the writers have used it to test columns packed with shale aggregate. The results in Table IV include for comparison unpublished data of one of the authors obtained in the Chemistry Department of Columbia University.

The shale aggregate packing is more efficient than the other packings tested. It is almost twice as efficient as the Fenske helices or the Stedman wire gauze packing. The liquid holdup per plate is about the same for all the columns tested, being slightly less for columns packed with glass helices. However, the efficiency varies by a factor of three for the different packings. With regard to throughput, the shale aggregate columns compare favourably with the glass helix columns. Both have high flooding velocities. The back pressure is higher in the aggregate columns. However, the higher efficiency of the aggregate will partly compensate for this, as shorter columns can be used. Further, it should be mentioned that the vapour velocity in most chemical exchange processes is limited by the solubility of gas or salt and the back pressure may be negligible. The results indicate that the new packing has application in chemical exchange processes where water solutions are used.

Discussion

The expanded shale aggregate has a large surface area on which liquids, including water, spread easily. This wetting property of the aggregate is due in part to the chemical, and in part to the physical, nature of the surface. A thin film of water is absorbed on the packing. This film can be removed by a stream of dry air. Although this absorbed liquid adds to the holdup of a packed column, it prevents a film of grease from forming and makes complete wetting of the packing possible under most conditions. The high efficiency of the shale aggregate packing with water systems is due in part to this factor. The efficient wetting of the packing also reduces channelling of the liquid and makes possible much higher flooding velocities.

The shale aggregate has several advantages over other cheap aggregate packings such as carborundum and corundum. It is very light weight and is easily supported in a column. It has a higher percentage of free space; this means a lower back pressure and a higher throughput. Towers 12 ft. in diameter and up to 300 ft. in length are used in the industry both for hydrocarbon and water systems. The high towers are required because of the low efficiency of the cheap packing materials available. It may be that with cheap aggregate packing available in small sizes much shorter columns could be used.

The packing was developed primarily for the further concentration of O^{18} by the distillation of water. A three stage cascade system has been designed and is now under construction.

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